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Isomerization of Bicyclo(2.2.1)-2,5-heptadiene to Cycloheptatriene

Here is a completely new reaction in organic chemistry, made practicable on an industrial scale by the availability of pure bicycloheptadiene

DEVERAL methods have been used to make 1,3,5-cycloheptatriene (CHT). It was first prepared over 60 years ago by Merling (9) and Ladenberg (8) through exhaustive methylation of tropidine. Willstätter (10) at the turn of the century, synthesized cycloheptatriene by systematic degradation of cycloheptanone. More recently Doering and Knox (5) made it by photochemical reaction of benzene with azomethane. These methods are laborious and give very low yields.

The thermal treatment of nonaromatic hydrocarbons often converts them to aromatics. Thus, it is surprising that when bicyclo(2.2.1)-2,5-heptadiene (BCH) is subjected to temperatures of approximately 400° to 475° C. in the vapor state at short residence times, a ring expansion to cycloheptatriene (4), a nonaromatic isomer, takes place. This simple vapor phase thermal isomerization technique has made possible production in quantities heretofore unavailable for organic synthesis.

Cycloheptatriene and toluene result from isomerization of the bicycloheptadiene ring; cyclopentadiene and acetylene, from a reversal of the Diels-Alder type reaction by which bicycloheptadiene is prepared. Some condensation products of higher molecular weight are obtained also.

Mechanism of Isomerization

The isomerization of bicycloheptadiene to cycloheptatriene formally involves the rupture of two carbon-carbon bonds and the formation of one.

A path from bicycloheptadiene to cycloheptatriene may be homolytic fission of the methano bridge to give a diradical, stabilization by collapse to norcaradiene, and valence tautomerization to cycloheptatriene.

Homolytic fission of the methano bridge is favored because the resulting diradical is partly allylic and thus stabilized by resonance. Rupture of the methano bridge also relieves con-

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siderable strain and allows the allylic (bridgehead) carbons to assume a more nearly tetrahedral form, bringing the methylene radical into suitable position for bond formation by electron pairing to give norcaradiene.

Toluene is also formed from the diradical, in this case by a 1,2-shift of the hydrogen bonded to the carbon carrying the methylene radical. As this requires additional energy, the easier course of collapse to cycloheptatriene proceeds predominantly at the temperatures involved.

An alternative mechanism involves cleavage of both carbon-carbon bonds of the methano bridge to give a methylene diradical joined to benzene as a π -complex. The methylene diradical may then become localized on a pair of joined carbons to produce norcaradiene, which converts to cycloheptatriene.

Apparatus

A typical continuous vapor phase reaction unit (Figure 1) was comprised of a feed system, vaporizer, and unpacked stainless steel tubular reactor electrically heated, and a product recovery system. Steel is a suitable material of construction; copper or copper alloys should be avoided, as unstable acetylides may be formed. In the recovery system the reactor effluent was cooled to tap water temperature in a water-cooled stainless steel heat exchanger, vapor and gas from this step were passed through a carbon dioxide(s)-acetone cold trap, and the exit gas was measured continuously with a wet-test meter. Material balances of ± 2 to 3% are easily obtained.

Feed System. Bicycloheptadiene was pumped continuously from a feed reservoir with a Model 1/2 Zenith gear metering pump. The reservoir consisted of a graduated cylinder, equipped with a buret-type side arm so that feed rate checks could be taken over short intervals during a run.

Vaporizer. The bicycloheptadiene vaporizer consisted of a small heat exchanger with steam at 100 p.s.i.g. in a central coil and around the shell. Its high surface area and low skin temperature provided smooth vaporization without decomposition. This unit was mounted horizontally and equipped with a drain valve for clean-out. An electrically heated vaporizer is suitable, but must be sized more carefully, to avoid high skin temperatures.

Reactor. The reactor tube consisted of a stainless steel pipe (1 inch in inside diameter and 30 inches long) mounted vertically in a four-section electric furnace. A thermowell 0.25 inch in outside diameter extended longitudinally the entire length of the tube. Thermocouples within this well recorded the temperature profile of the tube. Temperature control was provided by a





Figure 2. Infrared absorption spectra

thermocouple located in each of the four sections of the Hevi-Duty furnace; these were connected to a Celectray unit which provided automatic temperature control at predetermined settings.

The data in Table I were obtained using a steel reactor tube with a constant temperature zone volume of 320 ml.; the data in Table II, with a stainless steel reactor tube with an actual heated length of 26 inches and an estimated constant temperature zone volume of 313 ml. for residence time calculations.

Product Recovery. In one recovery system, reactor effluent at 400° to 475° C. was passed into the shell of a water-cooled heat exchanger which reduced the temperature to about 20° C. Liquid condensate accumulated here and was drained periodically. Gas and uncondensed vapor were passed through a carbon dioxide(s)-acetone cold trap where cyclopentadiene was condensed; the acetylene was passed through a wettest meter and vented.

Methods of Analysis

Analytical data for the liquid products presented in Table I were determined from the infrared absorption spectra. Infrared spectra of bicycloheptadiene and cycloheptatriene are presented in Figure 2; infrared spectra of cyclopentadiene, dicyclopentadiene, and toluene have been published (2). The spectra of the five compounds in carbon disulfide solution were recorded. These compounds have intense absorption bands from 7 to 15 microns, that make quantitative analysis relatively easy.

An absorption band that had minimum absorption from the other components was chosen as an analysis band for each compound. For analysis, the infrared spectrum of the liquid product in carbon disulfide solution was obtained and the percentage composition of each component derived by comparison of the absorbance of each band against the absorbance of the same band in the standard spectrum. Such analysis assumes adherence to Beer's law and does not account for absorbance of the other components. However, experience has shown the results to be generally accurate to about $\pm 5\%$.

The acetylene content of noncondensable gas was determined by the Texas Co. method (7), which involves titration of the nitric acid liberated from the reaction of acetylene and silver nitrate.

Analytical data in Table II were obtained by gas-liquid chromatography (GLC). The liquid product was analyzed at the following conditions:

170 ns- re-
per

Percentage composition was calculated by comparing the area under each peak to the total area under all peaks. The emergence time of each material was determined by passing pure standards through the column at the same operating conditions. This yields results accurate to about $\pm 3\%$ of the amount present.

Experimental Data

A typical set of experimental data obtained with the continuous vapor phase reaction is shown in Table I. Thefeed was preheated to 200° to 300° C. and made to react at 400° , 425° , and 450° C. The residence time ranged from 1 to 28 seconds. Infrared spectroscopic analyses were used to determine the composition of the liquid product. The data shown in Table II were obtained in a second reaction system; these runs were of greater duration, the product was fractionally distilled, and

Table I. Thermal Isomerization of Bicycloheptadiene to Cycloheptatriene

Reaction Conditions											BCH					Conv./ Pass
Run	Run time,	Feed rate, g /min	BCH fed, moles	Res. time,	Reac- tion temp.,	BCH	Reactio	n Produ	ct, Mole	CHT	Con- ver- sion,	Y CoHe	ields o Mo	f Product ble %	s,	to CHT, Mole
1	60	1.30	0.847	21.9	350	0.847			•••		0			••••	•••	0
2 3 4 5 6	30 30 30 60 60	2.97 2.83 1.90 1.33 0.97	0.968 0.925 0.620 0.870 0.631	8.9 9.3 14.0 23.3 27.3	400 400 400 400 400	0.870 0.794 0.510 0.636 0.407	0.031 0.046 0.046 0.062 0.081	0.026 0.075 0.059 0.079 0.108	0 0 0 0.017	0.047 0.054 0.055 0.122 0.102	10 14 18 27 36	31 35 42 26 35	27 57 53 34 46	0 0 0 7.2	48 41 50 52 44	5 6 9 14 16
7 8 9 10	31 30 60 60	2.77 1.73 1.42 0.93	0.935 0.565 0.925 0.608	9.2 14.8 18.0 27.5	425 425 425 425	0.574 0.276 0.310 0.110	0.142 0.119 0.235 0.161	0.182 0.157 0.273 0.210	0.024 0.014 0.023 0.014	0.148 0.113 0.294 0.230	38 51 66 82	39 41 38 32	50 54 44 42	6.7 4.8 3.8 2.8	41 39 48 46	16 20 32 37
11 12 13 14 15	10 11 20 30 117	22.30 12.55 5.40 2.33 1.31	2.42 1.50 1.17 0.762 1.66	1.1 2.0 4.6 10.6 18.8	450 450 450 450 450	2.18 1.28 0.664 0.157 0.137	0.096 0.119 0.204 0.238 0.680	0.169 0.142 0.258 0.282 0.670	0 0 0.018 0	0.120 0.073 0.239 0.281 0.753	10 15 43 79 92	40 54 40 39 45	70 65 51 47 44	0 0 3.0 0	50 33 47 46 49	5 20 36 45

CYCLOHEPTATRIENE





the fractions were analyzed by gasliquid chromatography. The effect of residence time on conversion of bicycloheptadiene and resultant cycloheptatriene yield at 400°, 425°, and 450° C. is shown in Figure 3. In all cases bicycloheptadiene conversion increases with increased residence time, while cycloheptatriene yields remain essentially constant at about 45 mole %. Figure 4 shows the effect of temperature on bicycloheptadiene conversion and cycloheptatriene yield at residence times of 5 and 10 seconds. Bicycloheptadiene conversion is essentially complete at 475° C. under these conditions of high throughput. The cycloheptatriene yield remained constant, at about 45 mole %. from 400° to 450° C. At 475° C., where bicycloheptadiene conversion was essentially complete, the yield declined to about 35 to 37 mole %. Analyt-

ical procedures and product work-up were not identical in the latter runs.

Laboratory-Scale Preparation of Cycloheptatriene

For laboratory-scale, where recycle of unconverted bicycloheptadiene is not practical, preferred conditions should consist of as high a conversion level and throughput rate as are consistent with good cycloheptatriene yields. Cycloheptatriene yield declines but little over the range of residence times and reaction temperatures shown in Figures 3 and 4. Thus, with the apparatus shown in Figure 1 and the conditions of run 3 (Table II)i.e., 5 seconds' residence time and 475° C. reaction temperature-cycloheptatriene amounted to 100 grams per hour. As bicycloheptadiene conversion at 9 seconds was 99% and at 5 seconds was

95%, higher throughput rates with accompanying higher cycloheptatriene makes per pass may still be possible before bicycloheptadiene conversion is reduced below a practical level. These preferred conditions for high conversion of bicycloheptadiene simplify the recovery of cycloheptatriene from the reaction product, as separation of cycloheptatriene from larger amounts of unreacted bicycloheptadiene is avoided.

Work-Up of Product

An acceptable product was obtained under atmospheric conditions in a 40tray Oldershaw column (Figure 5 and Table III). In this instance 74% of the cycloheptatriene was recovered as a fraction of 87 weight % purity; 4% of toluene and 9 weight % of cyclopentadiene resulting from cracking of dicyclopentadiene in the kettle were also present. In another case using only a 20-plate Oldershaw column (run 5, Table II) 89 weight % of the cyclo-

Table II. Thermal Isomerization of Bicycloheptadiene

(313-ml. reactor volume)

	<u>. </u>	Run Cor	nditions	·				Vielde of Dro	ducto Mal	. 67		BCH Conv./
Deen	Run	BCH,	Res.	T	BCH	Hearry Ende						- Pass to
No.	hours	g. led/ hr.	sec.	°C.	Conv., %	C_2H_2	$\mathrm{C}_5\mathbf{H}_6$	Toluene	\mathbf{CHT}	Mole % ^a	Wt. %b	Mole %
1	4.86	159	8.6	475	99	41.0	50.0	12.0	34.5	3.5	5.0	34
2	6.47	159	8.6	475	99	42.5	35.0	12.0	35.5	17.5	14.0	35
3	3.58	279	5.0	475	95	40.0	47.0	8.5	37.0	7.5	8.5	35
4	6.35	162	8.9	450	88	38.5	37.0	6.5	39.0	17.5	17.5	34
5	4.03	285	5.1	450	71	39.0	39.0	4.5	37.0	19.5	19.5	26
a 100 -	- (CHT +	- toluene +	cyclopen	tadiene).	^b Heavy e	ends grams	÷ BCH co	onverted gram	s (weight v	ield loss of B(CH)	



heptatriene formed was recovered in a fraction containing 89 weight % cycloheptatriene, 9 weight % toluene, and only 2 weight % cyclopentadiene. Better results can be obtained by vacuum distillation at a pressure chosen to limit the maximum kettle temperature to 90°C. Higher kettle temperatures should be avoided-dicyclopentadiene in the re-

action product reverts to cyclopentadiene and upsets column operation.

was

obtained

Cycloheptatriene resinifies on exposure to air. Addition of an oxidation inhibitor reduces this tendency.

Table IV summarizes some physical constants of the materials involved in recovery of cycloheptatriene from the reaction product.

		Analysis of $Fractions^a$									
Boiling Range, °C. at 630 Mm.	Wt. of Still Charge	Cyclo + dicyclo	BCH	Toluene	CHT	Xylene	Distribution of CHT, % of Total				
36- 83 83- 90 90-104 104-108	13.8 5.1 24.9	(74) (29) 11	(26) (71) 3	38	••• 48 97	•••	24.3				
104-108 109-131 Bottoms	3.3 11.5	4	•••	** •• ••	33	(63)	2.2				
* Parenthetica	al values of	otained by infr	ared spect	roscopy;	other valu	les by GLC					
	Tab	ole IV. Sum	mary of	Physical	Properti	es					
Physical Cy Properties		heptatriene CHT	Tolu	ene	Bicyclohe BC	ptadiene H	Cyclo- pentadiene				
Molecular weigh Boiling point, ° C	116–1 116 a 117 a 115.5 109–1 60.5	92.13 18 at 760 mm. tt 724 mm. ^a tt 749 mm. ^a at 760 mm. ^b 11 at 630 mm. at 122 mm. ^c	92. 110.6 at 104 at 6	13 760 mm. 30 mm.	92. 89.5 at 7 83 at 63	13 60 mm. 30 mm.	66.05 41 at 760 mm. 36 at 630 mm.				
Melting point, ° Density, g./cc. Refractive index	C. 0.887	-79.49 ^b 6 (18.5° C.)ª	 0.866(95 20° C.)	— 19 0.903 (2	9.9 25° C.)	0.805 (19° C.)				
$n_{\rm D}$ Structural formu	' 1.520 1a	08 (25° C.)¢	1.4969 (CE	20° C.) Ia	1.4684 ((25° C.)	1.45 (20° C.)				
^a (3). ^b (7).	/=		/				<u> </u>				

Table III. Analysis of Fractions from Distillation Shown in Figure 5

Methods of Calculation

The data have been correlated using the functions calculated in the generally accepted manner.

- Bicycloheptadiene conversion, % = (moles bicycloheptadiene fed moles bicycloheptadiene remaining) \times 100 \div moles bicycloheptadiene fed
- Yield of cycloheptatriene, mole (moles cycloheptatriene formed) X 100 ÷ moles bicycloheptadiene consumed
- Residence time = reactor volume volume rate of gas fed calculated at nominal temperature and pressure of reactor tube. Reactions carried out at nominal pressure of 630 mm. of mercury

Conclusions

Cycloheptatriene can be prepared readily by vapor phase isomerization of bicycloheptadiene, available in industrial quantities of high purity from Shell Chemical Corp. In the range of reaction variables investigated bicycloheptadiene conversion increases with increasing reaction temperature and increased residence time. For reaction temperatures of 375° to 475° C. and residence times of 2 to 30 seconds, conversions of 0 to 100% were obtained. The cycloheptatriene yield essentially constant at 45 to 50 mole % over the range of variables, declined slightly under the more severe thermal treatment at 475° C. Cycloheptatriene of 89 weight % purity can be obtained by atmospheric distillation of the reaction product; the balance of the product fraction consisted of 9 weight % toluene and 2 weight % cyclopentadiene.

Acknowledgment

The authors thank their colleagues in the Shell Chemical Corp. and Shell Development Co. who assisted in the experimental and analytical work.

Literature Cited

- (1) Altieri, V. J., "Gas Analysis and Testing of Gaseous Materials," p. 329, American Gas Association, New York, 1945.
- (2) Am. Petroleum Inst. Research Project 44, Pittsburgh, Pa., "Catalog of Infrared Spectra Data," No. 308,
- 458, 460. ilstein, "Chemische-physikalische (3) Beilstein,
- Beilstein, "Chemische-physikalische Tabellen," Vol. 5, p. 280.
 Chirtel, J. S., Halper, W. M. (to Shell Development Co.), U. S. Patent 2,754,337 (July 10, 1956).
 Doering, W., Knox, L. H. (to Research Corp.), *Ibid.*, 2,647,081 (July 29, 1052) 28, 1953
- (6) Dryden, H. L., J. Am. Chem. Soc. 76, 2841 (1954).
- (7) Kohler, E. P., others, *ibid.*, **61**, 1057 (1939). (8) Ladenburg, A., Ann. 217, 74-149
- (1883)
- Merling, G., Ber. 24, 3108-26 (1891). Willstätter, R., Ann. 317, 204-66 (10)(1901).

RECEIVED for review October 14, 1957 ACCEPTED March 3, 1958

° (6).